

REMOVABLE, WATER-WHITENING RESISTANT PRESSURE SENSITIVE  
ADHESIVES

RELATED APPLICATION

[0001] The present application is a nonprovisional application claiming benefit of U.S. Patent Application Serial Number 60/413,846, filed 26 September 2002, entitled Removable Water-Whitening Resistant Pressure Sensitive Adhesives, the disclosures of which are hereby incorporated herein by reference.

BACKGROUND OF THE INVENTION

[0002] This invention relates to removable pressure sensitive adhesives based on aqueous emulsions. The removable pressure sensitive adhesives of the invention have enhanced resistance to water-whitening.

[0003] Removable pressure sensitive adhesives are used on a variety of products including labels, tapes, films, and the like, to enable the product to adhere to a substrate and then to later be removed from the substrate without difficulty and without leaving a stain or residue. To be suitable for such applications, the pressure sensitive adhesive must have good adhesion with low peel strength and must not exhibit a significant increase in adhesion over time. Optimally, the pressure sensitive adhesive should exhibit such physical properties on a variety of substrates. Typical commercially available aqueous acrylic emulsion pressure sensitive adhesives that are removable cannot be used with film facestocks which are used in outdoor applications. One outdoor application involves decorative decals which are applied to substrates such as glass. One technique for applying such a decorative decal to a substrate is to spray water on the adhesive and/or substrate so that the decal is slidably movable over the substrate for ease of positioning. Unfortunately, in such a technique, the aqueous acrylic emulsion adhesive film turns milky in contact with water. Another outdoor application involves protective films that are applied via adhesive to materials for construction projects where the film serves to protect the construction material until the construction project is completed. Exposure of the protective film covered construction materials to water or high humidity in outdoor

environments often results in the aqueous acrylic emulsion adhesive turning milky. For transparent filmstocks, this water-whitening results in an unsatisfactory appearance.

**[0004]** For a successful aqueous acrylic emulsion removable pressure sensitive adhesive to be used with decorative or protective films and decals in outdoor applications, the adhesive needs to exhibit good water resistance along with good anchorage of the adhesive to the film facestock to assure clean removability from the substrate. The current commercially available aqueous acrylic emulsion pressure sensitive adhesives which demonstrate good water-whitening resistance are permanent adhesives, i.e. those that leave an adhesive residue on the substrate if the facestock is removed. Currently available removable aqueous acrylic emulsion pressure sensitive adhesives which demonstrate good anchorage to the film also exhibit poor water-whitening resistance. Accordingly, there is a need for an aqueous acrylic emulsion pressure sensitive adhesive which exhibits both desired properties of removability and water-whitening resistance.

#### SUMMARY OF THE INVENTION

**[0005]** According to the invention, a removable, water-whitening resistant pressure sensitive adhesive (PSA) is provided comprising a crosslinked aqueous emulsion polymer comprising (a) at least one hydrophobic monomer selected from an alkyl (meth)acrylate ester of an alcohol wherein the alkyl portion of the alcohol is linear or branched and contains at least 4 carbon atoms, or a mixture of at least one styrenic monomer and at least one alkyl (meth)acrylate ester of an alcohol wherein the alkyl portion of the alcohol is linear or branched and contains at least 4 carbon atoms, wherein when a styrenic monomer is present, the styrenic monomer is present in an amount up to about 30 wt. % of the total hydrophobic monomer mixture; (b) at least about 2 wt. % of at least one hydrophilic monomer; (c) at least about 5 wt. % of at least one partially hydrophilic monomer selected from alkyl (meth)acrylate esters of an alcohol wherein the alkyl portion of the alcohol has 1 to 2 carbon atoms, N-vinyl-2-pyrrolidone, or mixtures thereof; wherein the crosslinked aqueous emulsion polymer is crosslinked with an effective amount of at least one polyfunctional aziridine crosslinker, and the wt. % of monomers (a), (b), and (c) are based on the total weight of monomers (a), (b), and (c).

**BRIEF DESCRIPTION OF THE DRAWINGS**  
**NOT APPLICABLE.**

**DETAILED DESCRIPTION OF THE INVENTION**

**[0006]** This invention provides aqueous emulsion pressure sensitive adhesives useful with decorative or protective films and decals in outdoor applications, the adhesive exhibiting removability from the substrate and good water resistance when subject to water or high humidity during use. The pressure sensitive adhesives of the invention have good adhesion with low peel strength. The face stock material having coated thereon the removable, water-whitening resistant pressure sensitive adhesive composition of the invention exhibit low peel adhesion with failure mode being essentially adhesive failure. The peel adhesion is dependent on the aqueous adhesive composition of the invention and the substrate. For example, the PSA compositions of the invention typically exhibit dry film peel values less than about 2.5 pounds per inch (431 N/m) peel force, preferably about 0.1 to about 2 pounds per inch (about 17.2 to about 345 N/m) peel force, with adhesive failure mode.

**[0007]** The removable pressure sensitive adhesives of the invention exhibit enhanced resistance to water-whitening. The extent of water-whitening can be determined visually by soaking the adhesive film in room temperature water for 24 hours and visually ranking the whitening of the adhesive.

**[0008]** The invention relates to a removable, water-whitening resistant pressure sensitive adhesive (PSA) comprising a crosslinked aqueous emulsion polymer comprising (a) at least one hydrophobic monomer selected from an alkyl (meth)acrylate ester of an alcohol wherein the alkyl portion of the alcohol is linear or branched and contains at least 4 carbon atoms, or a mixture of at least one styrenic monomer and at least one alkyl (meth)acrylate ester of an alcohol wherein the alkyl portion of the alcohol is linear or branched and contains at least 4 carbon atoms, wherein when a styrenic monomer is present, the styrenic monomer is present in an amount up to about 30 wt. % of the total hydrophobic monomer mixture; (b) at least about 2 wt. % of at least one hydrophilic monomer; and (c) at least about 5 wt. % of at least one partially hydrophilic monomer selected from alkyl (meth)acrylate esters of

an alcohol wherein the alkyl portion of the alcohol has 1 to 2 carbon atoms, N-vinyl-2-pyrrolidone, or mixtures thereof; wherein the crosslinked aqueous emulsion polymer is crosslinked with an effective amount of at least one polyfunctional aziridine crosslinker, and the wt. % of monomers (a), (b), and (c) are based on the total weight of monomers (a), (b), and (c).

**[0009]** Hydrophobic monomers that can be employed according to the invention include at least one alkyl (meth)acrylate ester of an alcohol wherein the alkyl portion of the alcohol is linear or branched and contains at least 4 carbon atoms, and mixtures of at least one styrenic monomer and at least one alkyl (meth)acrylate ester of an alcohol wherein the alkyl portion of the alcohol is linear or branched and contains at least 4 carbon atoms. As used herein, the term alkyl (meth)acrylate includes both alkyl acrylates and alkyl methacrylates. The alkyl groups of the alkyl acrylate or alkyl methacrylate monomers are preferably linear or branched alkyl radicals having from 4 to about 14 carbon atoms, more preferably from 4 to about 10 carbon atoms, and most preferably from 4 to about 8 carbon atoms. Examples of suitable alkyl acrylates and alkyl methacrylates include, but are not limited to, isooctyl acrylate, 4-methyl-2-pentyl acrylate, 2-methyl-butyl acrylate, isoamyl acrylate, sec-butyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate, isodecyl methacrylate, isononyl acrylate, isodecyl acrylate, and the like, singly or in mixtures of two or more. Examples of suitable styrenic monomers include, but are not limited to, styrene,  $\alpha$ -methyl styrene, vinyl toluene, t-butyl styrene, dimethyl styrene, and the like, singly or in mixtures of two or more.

**[0010]** The currently preferred alkyl acrylate or alkyl methacrylate ester monomers are 2-ethylhexyl acrylate, n-butyl acrylate, and mixtures thereof. The currently preferred styrenic monomer is styrene.

**[0011]** The amount of hydrophobic monomers based on the total weight of monomers (a), (b), and (c) is preferably about 50 to about 90 wt. %, more preferably about 70 to about 90 wt. %, and most preferably about 70 to about 85 wt. %.

**[0012]** When a styrenic monomer is employed in the invention, the amount of styrenic monomer can conveniently be expressed as a wt. % of the total hydrophobic monomer mixture. When a styrenic monomer is employed, the amount of styrenic monomer is up to about 30 wt. %, preferably about 5 to about 30 wt. %, and most preferably about 5 to about 10 wt. %.

and more preferably about 10 to about 20 wt. %, of the total hydrophobic monomer mixture.

**[0013]** Hydrophilic monomers that can be employed according to the invention are monomers that are copolymerizable with the hydrophobic monomer and that are water soluble. The hydrophilic monomers are selected from monoolefinic monocarboxylic acids, monoolefinic dicarboxylic acids, 2-hydroxyethyl acrylate, or mixtures thereof.

**[0014]** Examples of suitable hydrophilic monomers include, but are not limited to, acrylic acid, methacrylic acid, fumaric acid, maleic acid, itaconic acid, crotonic acid, oligomeric acrylic acid, 2-hydroxyethyl acrylate, and mixtures thereof. The currently preferred hydrophilic monomers are acrylic acid, 2-hydroxyethyl acrylate, methacrylic acid, and mixtures thereof.

**[0015]** The amount of hydrophilic monomers based on the total weight of monomers (a), (b), and (c) is at least about 2 wt. %, preferably about 2 to about 10 wt. %, more preferably about 3 to about 10 wt. %, and most preferably about 3 to about 8 wt. %.

**[0016]** Partially hydrophilic monomers that can be employed according to the invention include alkyl (meth)acrylate esters of an alcohol wherein the alkyl portion of the alcohol has 1 to 2 carbon atoms, N-vinyl-2-pyrrolidone, or mixtures thereof. The partially hydrophilic monomers can also be referred to as partially water soluble monomers.

**[0017]** Examples of suitable partially hydrophilic monomers include methyl acrylate, methyl methacrylate, ethyl acrylate, N-vinyl-2-pyrrolidone, and mixtures thereof. The currently preferred partially hydrophilic monomers are methyl acrylate, methyl methacrylate, and mixtures thereof, with methyl acrylate being currently most preferred.

**[0018]** The amount of partially hydrophilic monomers based on the total weight of monomers (a), (b), and (c) is at least about 5 wt. %, preferably about 5 to about 25 wt. %, and more preferably about 8 to about 20 wt. %.

**[0019]** The process for the preparation of the removable, water-whitening resistant pressure sensitive adhesives of the invention uses, and the crosslinked aqueous emulsion polymer of the invention further comprises, a surfactant selected

from a non-polymerizable surfactant, a polymerizable surfactant, or mixtures thereof. When a non-polymerizable emulsifier, i.e. surfactant, is used, the non-polymerizable surfactants that can be employed include anionic, nonionic, cationic, or amphoteric emulsifiers and mixtures thereof. Ionic emulsifiers are currently preferred, with anionic emulsifiers being currently most preferred. Examples of suitable anionic emulsifiers include, but are not limited to, alkyl aryl sulfonates (e.g. sodium dodecylbenzene sulfonate), alkyl sulfates (e.g. sodium dodecyl sulfate, ammonium dodecyl sulfate), sulfates of ethoxylated alcohols (e.g. sodium lauryl ether sulfate), sulfates and sulfonates of ethoxylated alkylphenols (e.g. ammonium nonylphenol ether (EO=30) sulfate, sodium salt of alkylaryl polyether sulfonates), sulfosuccinates (e.g. sodium dioctyl sulfosuccinate), diphenyl sulfonates (e.g. sodium dodecyl diphenyloxide disulfonate), and mixtures thereof. Examples of suitable nonionic emulsifiers include, but are not limited to, ethoxylated alcohols (e.g. ethoxylated oleyl alcohol), ethoxylated alkylphenols (e.g. nonylphenol ethoxylate), and mixtures thereof. Examples of suitable cationic emulsifiers include, but are not limited to, ethoxylated fatty amines (e.g. ethoxylated tallow amine).

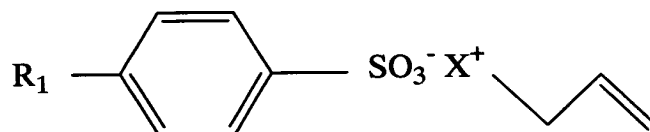
**[0020]** When used alone, the typical concentration of non-polymerizable surfactant is based on the total weight of monomers (a), (b), and (c) and is about 0.1 to about 5 wt. %, preferably about 0.5 to about 3 wt. %. When a non-polymerizable surfactant is used in conjunction with a polymerizable surfactant, the typical total concentration of surfactant is based on the total weight of monomers (a), (b), and (c) and is about 0.1 to about 5 wt. %, preferably about 0.5 to about 3 wt. %.

**[0021]** Water-soluble or water-dispersible polymerizable surfactants having a terminal allyl amine moiety that can be employed according to the invention include those polymerizable surfactants disclosed in U.S. Patent No. 5,928,783 and U.S. Patent No. 6,239,240, which are incorporated herein by reference in their entirety. Preferably, the polymerizable surfactants of the invention contain a hydrophilic portion selected from a sulfonate allyl amine moiety, a sulfate allyl amine moiety, or a phosphate allyl amine moiety, and a hydrophobic portion selected from -R, or a group having the formula  $\text{RO}-(\text{CH}_2\text{CH}_2\text{O})_n-$ ; wherein R is an alkyl group or an alkyl-substituted phenyl group wherein the alkyl group has 1 to 20 carbon atoms, preferably 10 to 18 carbon atoms, and n is an integer from 2 to 100, preferably 2 to

15. The hydrophilic portion and the hydrophobic portion are connected by means of a covalent bond. Combinations of such polymerizable surfactants can be used in preparing the polymers of the invention. The water-soluble or water-dispersible polymerizable surfactants having a terminal allyl amine moiety useful in the invention are available from Stepan Company under the Polystep® NMS trademark.

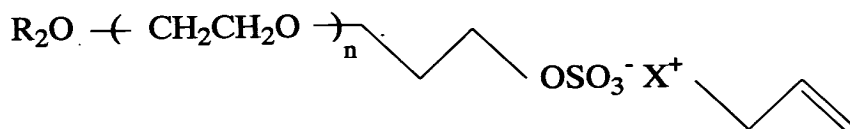
**[0022]** Suitable water-soluble or water-dispersible polymerizable surfactants having a terminal allyl amine moiety include, but are not limited to, the following examples.

**[0023]** A preferred polymerizable surfactant is an allyl amine salt of an alkyl benzene sulfonate having the formula



wherein  $\text{R}_1$  is an alkyl group having 1 to 20 carbon atoms, preferably 10 to 18 carbon atoms, and  $\text{X}^+$  is selected from  $^+\text{NH}_3$ ,  $^+\text{NH}_2\text{R}_4$ , or  $^+\text{NHR}_4\text{R}_5$ , wherein  $\text{R}_4$  and  $\text{R}_5$  are independently selected from  $\text{C}_1$ - $\text{C}_4$  alkyl or hydroxyalkyl groups.  $\text{X}^+$  is preferably  $^+\text{NH}_3$ . An example of a polymerizable surfactant of this type is an allyl amine salt of dodecylbenzene sulfonate.

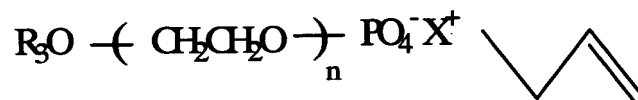
**[0024]** Another preferred polymerizable surfactant is an allyl amine salt of an alkyl ether sulfate having the formula



wherein  $\text{R}_2$  is an alkyl group having 1 to 20 carbon atoms, preferably 10 to 18 carbon atoms,  $n$  is an integer from 2 to 100, preferably 2 to 15, and  $\text{X}^+$  is selected from  $\text{NH}_3^+$ ,  $^+\text{NH}_2\text{R}_4$ , or  $^+\text{NHR}_4\text{R}_5$ , wherein  $\text{R}_4$  and  $\text{R}_5$  are

independently selected from C<sub>1</sub>-C<sub>4</sub> alkyl or hydroxyalkyl groups. X<sup>+</sup> is preferably <sup>+</sup>NH<sub>3</sub>. An example of a polymerizable surfactant of this type is an allyl amine salt of laureth sulfate.

**[0025]** Another preferred polymerizable surfactant is an allyl amine salt of a phosphate ester having the formula



wherein R<sub>3</sub> is an alkyl or alkyl-substituted phenyl group wherein the alkyl group has 1 to 20 carbon atoms, n is an integer from 2 to 100, preferably 2 to 15, and X<sup>+</sup> is selected from <sup>+</sup>NH<sub>3</sub>, <sup>+</sup>NH<sub>2</sub>R<sub>4</sub>, or <sup>+</sup>NHR<sub>4</sub>R<sub>5</sub>, wherein R<sub>4</sub> and R<sub>5</sub> are independently selected from C<sub>1</sub>-C<sub>4</sub> alkyl or hydroxyalkyl groups. X<sup>+</sup> is preferably <sup>+</sup>NH<sub>3</sub>. An example of a polymerizable surfactant of this type is an allyl amine salt of nonylphenol ethoxylate (9 moles EO) phosphate ester.

**[0026]** Yet another preferred polymerizable surfactant is an allyl amine salt of a sulfate having the formula

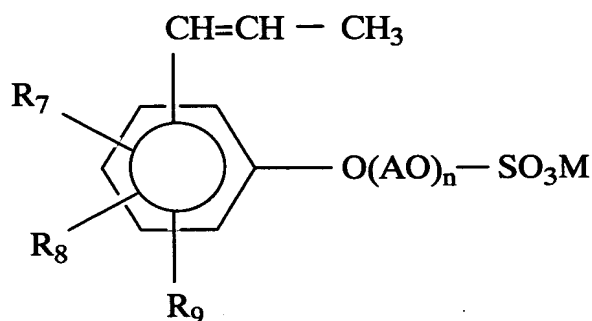


wherein R<sub>6</sub> is an alkyl group having 6 to 20 carbon atoms, preferably 10 to 18 carbon atoms, and X<sup>+</sup> is selected from <sup>+</sup>NH<sub>3</sub>, <sup>+</sup>NH<sub>2</sub>R<sub>4</sub>, or <sup>+</sup>NHR<sub>4</sub>R<sub>5</sub>, wherein R<sub>4</sub> and R<sub>5</sub> are independently selected from C<sub>1</sub>-C<sub>4</sub> alkyl or hydroxyalkyl groups. X<sup>+</sup> is preferably <sup>+</sup>NH<sub>3</sub>.

**[0027]** The substituted phenyl compounds having at least one alkenyl substituent that can be employed as water-soluble or water dispersible polymerizable surfactants according to the invention include those disclosed in U.S. Patent No. 5,332,854, which is incorporated herein by reference in its entirety.



**[0028]** Suitable substituted phenyl compounds having at least one alkenyl substituent include compounds having the formula:



wherein  $R_7$  is an alkyl, alkenyl or aralkyl group containing 6 to 18 carbon atoms;  $R_8$  is a hydrogen atom or an alkyl, alkenyl or aralkyl group containing 6 to 18 carbon atoms;  $R_9$  is a hydrogen atom or a propenyl group; A is an unsubstituted or substituted alkylene group of 2 to 4 carbon atoms; n is an integer of 1 to about 200, preferably 2 to about 100; and M is an alkali metal, an ammonium ion or an alkanolamine residue.

**[0029]** In the substituted phenyl compounds of the invention, the alkyl, alkenyl and aralkyl groups of  $R_7$  and  $R_8$  are independently selected and may be the same or different. Suitable alkyl groups include, but are not limited to, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl and octadecyl. Suitable alkenyl groups include, but are not limited to, hexenyl, heptenyl, octenyl, nonenyl, decenyl, undecenyl, dodecenyl, tridecenyl, tetradecenyl, pentadecenyl, hexadecenyl, heptadecenyl and octadecenyl. Suitable aralkyl groups include, but are not limited to, styryl, benzyl and cumyl.

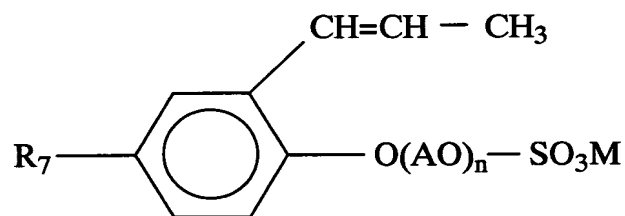
**[0030]** The propenyl group may occur as trans- and cis-isomers. For the purposes of the present invention, these isomers may be used independently or as a mixture.

**[0031]** For A, suitable unsubstituted or substituted alkylene groups include, for example, ethylene, propylene, butylene, and isobutylene. The

polyoxyalkylene group  $-(AO)_n-$  can be a homo-, block or random polymer, or a mixture thereof.

**[0032]** The conditions of the reaction for producing the substituted phenyl surfactant of the present invention are not critical. For example, the substituted phenyl surfactant can be produced by adding an alkylene oxide such as ethylene oxide (EO) or propylene oxide (PO) to an alkylated propenyl phenol in the usual manner, sulfating the adduct with a sulfating agent such as sulfuric acid, sulfamic acid, chlorosulfonic acid, or the like, followed by neutralizing with an alkaline substance.

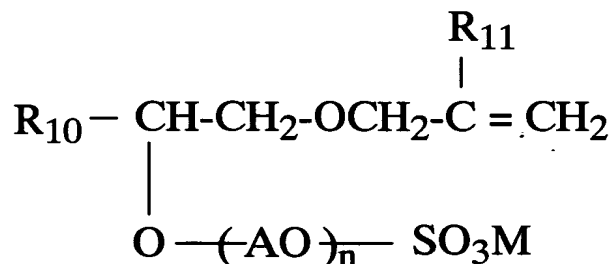
**[0033]** A currently preferred group of substituted phenyl compounds are those compounds having the formula:



wherein  $R_7$ , A, M and n is as defined above. More preferred compounds are those wherein  $R_7$  is alkyl, A is ethylene ( $-\text{CH}_2\text{CH}_2-$ ), and M is alkali metal or ammonium. Most preferred compounds are those wherein M is ammonium,  $R_7$  is nonyl, and n is about 10 to about 30, such as the compounds available from Dai-Ichi Kogyo Seiyaku Co., Ltd. (Tokyo, Japan) under the tradename Hitenol BC.

**[0034]** The polyoxyalkylene-1-(allyloxymethyl) alkyl ether sulfate salt compounds that can be employed as water-soluble or water-dispersible polymerizable surfactants according to the invention include those disclosed in Japanese Patent No. JP 2596441 B2 (Dai-Ichi Kogyo Seiyaku Co., Ltd.).

**[0035]** Suitable polyoxyalkylene-1-(allyloxymethyl) alkyl ether sulfate salt compounds include compounds having the formula:

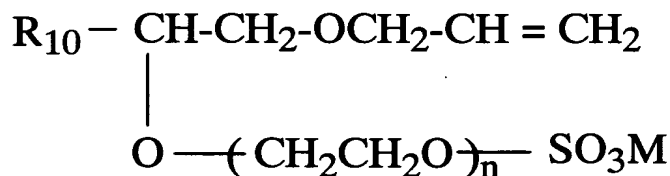


wherein R<sub>10</sub> is a linear or branched alkyl group containing 8 to 30 carbon atoms, preferably 8 to 14 carbon atoms, and more preferably 10 to 12 carbon atoms; R<sub>11</sub> is hydrogen or methyl, preferably hydrogen; A is an unsubstituted or substituted alkylene group having 2 to 4 carbon atoms; n is 0 or an integer of 1 to about 200, preferably 2 to about 100, more preferably 2 to about 30; and M is an alkali metal, an ammonium ion, or an alkanolamine residue. Examples of alkanolamine residues include monoethanolamine, triethanolamine, and the like.

**[0036]** For A, suitable unsubstituted or substituted alkylene groups include, for example, ethylene, propylene, butylene, and isobutylene. The polyoxyalkylene group -(AO)<sub>n</sub>- can be a homo-, block or random polymer, or a mixture thereof.

**[0037]** The polyoxyalkylene-1-(allyloxymethyl) alkyl ether sulfate salt compounds of the invention can be prepared according to the methods described in Japanese Patent No. JP 2596441 B2.

**[0038]** A currently preferred group of polyoxyalkylene-1-(allyloxymethyl) alkyl ether sulfate salt compounds are those compounds having the formula:



wherein R<sub>10</sub> is an alkyl group containing 8 to 14 carbon atoms, and preferably

10 to 12 carbon atoms; n is an integer of 1 to about 200, preferably 2 to about 100, more preferably 2 to about 30; and M is an alkali metal, an ammonium ion, or an alkanolamine residue. More preferred compounds are those wherein R<sub>10</sub> is a decyl or dodecyl group, n is 5 to 10, and M is NH<sub>4</sub>, such as the compounds available from Dai-Ichi Kogyo Seiyaku Co., Ltd. (Tokyo, Japan) under the trademark Hitenol® KH.

**[0039]** When used, the total amount of water-soluble or water-dispersible polymerizable surfactant utilized in the preparation of the removable, water-whitening resistant pressure sensitive adhesives of the invention is based on the total weight of monomers (a), (b), and (c) and is about 0.1 to about 5 wt. %, preferably about 0.5 to about 3 wt. %.

**[0040]** It is currently preferred that the surfactant used for the preparation of the crosslinked aqueous emulsion polymer of the invention to be used in the removable, water-whitening resistant pressure sensitive adhesives of the invention comprises at least one ionic non-polymerizable surfactant, at least one polymerizable surfactant, or mixtures thereof. In one preferred embodiment, the surfactant is a mixture of at least one non-polymerizable ionic surfactant and at least one non-polymerizable non-ionic surfactant. In another preferred embodiment, the surfactant is a polymerizable surfactant.

**[0041]** The process for the preparation of the removable, water-whitening resistant pressure sensitive adhesives of the invention also utilizes at least one water-soluble polymerization initiator. Any conventional water-soluble polymerization initiator that is normally acceptable for emulsion polymerization of acrylate monomers may be used and such polymerization initiators are well known in the art. The typical concentration of water-soluble polymerization initiators is about 0.01 wt. % to about 1 wt. %, preferably about 0.01 wt. % to about 0.5 wt. %, of the total weight of monomers (a), (b), (c), and (d) charged in the pre-emulsion. The water soluble polymerization initiators can be used alone or used in combination with one or more conventional reducing agents, such as bisulfites, metabisulfites, ascorbic acid, sodium formaldehyde sulfoxylate, ferrous sulfate, ferrous ammonium sulfate, ferric ethylenediamine-tetraacetic acid, and the like. Water-soluble polymerization

initiators that can be employed according to the invention include water soluble persulfates, peroxides, azo compounds and the like, and mixtures thereof. Examples of water soluble initiators include, but are not limited to, persulfates (e.g. potassium persulfate, and sodium persulfate), peroxides (e.g. hydrogen peroxide, and tert-butyl hydroperoxide), and azo compounds (e.g. 4,4'-azobis(4-cyano-pentanoic acid), V-501 from Wako Chemicals). Currently the preferred water soluble polymerization initiators are the persulfates, particularly potassium persulfate.

**[0042]** The polymerization can be initiated by any conventional method known to those skilled in the art, such as by application of heat or radiation. The method of initiation will be dependent on the water-soluble polymerization initiator used and will be readily apparent to those skilled in the art.

**[0043]** The water soluble polymerization initiator can be added to the polymerization reaction in any conventional manner known in the art. It is currently preferred to add a portion of the initiator to the initial reactor charge which comprises water, an effective amount of the water-soluble or water-dispersible polymerizable surfactant, and an initial amount of the polymerization initiator. The remainder of the initiator can be added continuously or incrementally during the emulsion polymerization. It is currently preferred to incrementally add the remaining initiator.

**[0044]** Following polymerization, the pH of the latex emulsion is adjusted by contacting the latex emulsion with a suitable base in an amount necessary to raise the pH to at least 6, preferably about 6.5 to about 9, and more preferably about 7 to about 8. Examples of suitable bases for adjusting the pH of the latex emulsion include alkali metal hydroxides, alkaline earth metal hydroxides, ammonium hydroxide, amines, and the like, and mixtures thereof. The currently preferred base for use in the invention is ammonium hydroxide.

**[0045]** The latex emulsion typically has a solids content of from about 40 to about 70 wt. %, and preferably about 45 to about 55 wt. %.

**[0046]** The particle size of the aqueous emulsion polymer is not critical provided the particle size is small enough to such that the water-whitening resistance is acceptable. The acceptable upper limit for particle size will depend on the monomer composition used in the polymerization and whether a polymerizable surfactant is used in the polymerization. For example, a mean particle size of 615 nm is acceptable

for a monomer composition of 50 2-EHA/32 BA/4 MMA/10 MA/1.5 MAA/2.5 AA with no polymerizable surfactant used. It is currently preferred, however, to select the monomer composition, surfactant and polymerization reactor operating conditions to result in a mean particle size of  $\leq 400$  nm.

**[0047]** The polymerization reaction can be conducted in any conventional reaction vessel capable of an emulsion polymerization.

**[0048]** The polymerization can be conducted at a temperature typical for emulsion polymerizations. The polymerization is preferably conducted at a temperature in the range of about 50°C to about 95°C, preferably in the range of about 60°C to about 85°C.

**[0049]** The polymerization time is that time needed to achieve the desired conversion based on the other reaction conditions, e.g. temperature profile, and reaction components, e.g. monomers, initiator, etc. The polymerization time will be readily apparent to those skilled in the art.

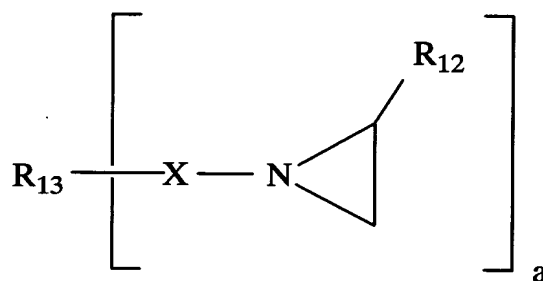
**[0050]** The crosslinking agent used in the PSA composition of the present invention is a polyfunctional aziridine compound. As used herein, a polyfunctional aziridine compound includes (a) compounds having two or more aziridine groups, and (b) compounds having at least two nitrogen atoms present wherein at least one of the nitrogen atoms is in an aziridine ring and one or more nitrogen atoms may be present in a side chain bonded to the aziridine nitrogen. It is currently preferred that the polyfunctional aziridine compounds are polyaziridine compounds having at least two aziridine groups.

**[0051]** Polyfunctional aziridine compounds that can be used for effecting crosslinking of the aqueous emulsion polymers of the invention containing pendent carboxyl functionality include, but are not limited to, the polyfunctional aziridines taught in U.S. Pat. Nos. 4,278,578, 4,605,698, and 4,645,789, all of which are incorporated herein by reference.

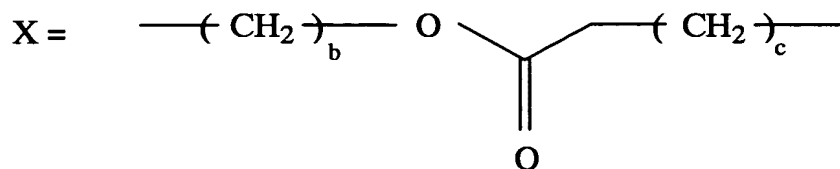
**[0052]** Suitable polyfunctional aziridine crosslinking agents include aziridine compounds having from 3 to 5 nitrogen atoms per molecule, and N-(aminoalkyl)-aziridines such as N-aminoethyl-N-aziridylethylamine, N,N-bis-2-aminopropyl-N-aziridylethylamine, and N-3,6,9-triazanonyl-aziridine. Other suitable polyfunctional aziridine crosslinkers include the trifunctional aziridine crosslinkers,

such as those sold under the trade designations: Crosslinker CX-100 (from NeoResins, part of Avecia Inc., Wilmington, MA) and Ionac® PFAZ-322, XAMA-2, and XAMA-7 (from Sybron Chemicals, Birmingham, NJ). Other examples of polyfunctional aziridine crosslinkers include bis and tris aziridines of di and tri acrylates of alkoxyated polyols, such as the tris aziridine of the triacrylate of the adduct of glycerol and 3.8 moles of propylene oxide; the bis aziridine of the diacrylate of the adduct of neopentyl glycol and 2 moles ethylene oxide, the bis aziridine of the diacrylate of the adduct of bisphenol A and 4 moles ethylene oxide and the tris aziridine of the triacrylate of the adduct of pentaerythritol and 4.7 moles of propylene oxide.

[0053] The preferred polyfunctional aziridine crosslinkers of the invention include those represented by the formula:



wherein  $\text{R}_{12}$  is hydrogen or an alkyl group having 1 to 10 carbon atoms, preferably 1 to 4 carbon atoms, which is optionally substituted by groups which do not interfere with the crosslinking reaction such as, but not limited to, nitro, halogen, hydroxy,  $\text{C}_1$  to  $\text{C}_{12}$  alkoxy and the like;  $\text{R}_{13}$  is an aliphatic radical having 1 to 30 carbon atoms, preferably 1 to 10, optionally substituted by hydroxy, halogen,  $\text{C}_1$  to  $\text{C}_{12}$  alkoxy and the like, or a direct bond; X is an alkylene group having 1 to 30 carbon atoms, optionally containing an ester group, an ether group, an amide group or a similar inert group; and "a" is 2 to 4. Preferred polyaziridines are those in which  $\text{R}_{12}$  is hydrogen, methyl, ethyl, propyl or butyl, X is represented by the formula



wherein b is 1 to 3 and c is 1 to 3, a is 2 to 3, and R<sub>13</sub> is a propylene radical or a 2-hydroxyethyl radical.

**[0054]** Examples of polyaziridines of the above formula for use in the invention include, but are not limited to, trimethylolpropane tris[([β]-N-aziridiny)propionate] (commercially available as Crosslinker CX-100 and Ionac® XAMA-2), pentaerythritol tris[([β]-N-aziridiny)propionate] (commercially available as Ionac® XAMA-7), trimethylolpropane tris[([β]-N-2-methyl-1-aziridiny)propionate] (commercially available as Inoac® PFAZ-322).

**[0055]** An effective amount of the polyfunctional aziridine compound used as the crosslinking agent in the PSA composition of the present invention is an amount to achieve sufficient crosslinking to produce the removable, water-whitening resistant PSAs of the invention. Typically, the effective amount of the polyfunctional aziridine compound used as the crosslinking agent in the PSA composition of the present invention is such that the amount of aziridine groups is at least 0.01 equivalents, preferably about 0.05 to about 5 equivalents, and more preferably about 0.1 to about 2 equivalents of aziridine groups in the polyfunctional aziridine compound per equivalent of carboxyl group present in the aqueous emulsion polymer, and which are derived from the total amount of monomers (a), (b), and (c) used in the production of the aqueous emulsion polymer.

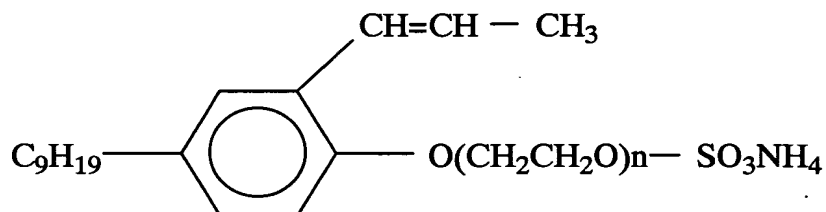
**[0056]** The polyfunctional aziridine compound used as the crosslinking agent in the PSA composition can be added to the aqueous emulsion polymer during the polymerization process, at the end of the polymerization process, or during the formulation of the pressure sensitive adhesive. It is currently preferred to add the polyfunctional aziridine compound during the formulation of the pressure sensitive adhesive.



## EXAMPLES

### ABBREVIATIONS AND SOURCE OF MATERIALS

<b>2-EHA:</b>	2-ethylhexyl acrylate; Ashland Inc.
<b>BA:</b>	butyl acrylate; Ashland Inc.
<b>MMA:</b>	methyl methacrylate; Ashland Inc.
<b>MA:</b>	methyl acrylate; Ashland Inc.
<b>AA:</b>	acrylic acid; Ashland Inc.
<b>MAA:</b>	methacrylic acid; Ashland Inc.
<b>CX-100:</b>	Crosslinker CX-100; trimethylolpropane tris[([β]-N-aziridinyl)-propionate]; NeoResins, part of Avecia Inc.
<b>Hitenol BC-2020:</b>	20 % active in water, n is about 20;



Dai-Ichi Kogyo Seiyaku Co., Ltd.

<b>PPS:</b>	potassium persulfate; Sigma-Aldrich Co.
<b>NH<sub>4</sub>OH:</b>	Ammonium hydroxide (28%); Sigma-Aldrich Co.
<b>AOT-75:</b>	sodium dioctyl sulfosuccinate (75% active); Cytec
<b>L-22:</b>	ammonium lauryl sulfate(30% active); Rhodia
<b>B-22:</b>	ammonium lauryl ether (EO=12) sulfate (30% active); Stepan
<b>FES-77:</b>	sodium lauryl ether (EO=30) sulfate (33% active); Cognis Corp.
<b>CO-660:</b>	Igepal CO 660 – nonyl phenol ethoxylate (10 moles EO); Rhodia
<b>BOPP:</b>	biaxially oriented polypropylene film; Intex
<b>PET:</b>	polyethylene terephthalate film; DuPont
<b>BDDM:</b>	butanediol dimethacrylate; Sigma-Aldrich Co.
<b>DS-4:</b>	sodium dodecylbenzene sulfonate (30% active); Rhodia
<b>SBC:</b>	sodium bicarbonate; Sigma-Aldrich Co.
<b>TBHP:</b>	tert-butyl hydroperoxide; Akzo Nobel

**F rmapon:** sodium formaldehyde sulfoxylate; Henkel

**Parolite:** zinc formaldehyde sulfoxylate; Henkel

#### EXAMPLE 1

**[0057]** In a 2L jacketed glass reactor equipped with a reflux condenser, thermocouple and four-blade agitator, 1000.0 g of polyacrylate latex was prepared. Monomer pre-emulsion was prepared by mixing 107.4 g water, 268.4 g 2-EHA, 171.8 g BA, 21.5 g MMA, 53.7 g MA, 8.1 g MAA and 13.4 g AA with 7.2 g B-22, 4.3 g CO-660 and 2.1 g AOT. The reactor was charged with 332.5 g water, 2.7 g PPS and 3.0 wt. % of the monomer pre-emulsion. The reactor was heated with water. When the temperature reached 79°C, continuous addition of the monomer pre-emulsion commenced at a rate of 3.13 g/min for 210 minutes. The temperature was maintained at 82°C and the polymerization charge agitated continuously from 250 – 450 rpm. After the pre-emulsion addition was complete, the reactor temperature was held at 82°C and agitated for an additional 40 minutes. The reactor temperature was cooled to 55°C after which 0.54 g TBHP and 0.43 g of Parolite were added to the reactor. After 15 minutes of agitation, the reactor was cooled to 30°C and 0.11 g Kathon LX biocide (Rohm and Haas) was added to the reactor and the pH was adjusted between 7-8 using 28% NH<sub>4</sub>OH aqueous solution.

#### EXAMPLE 2

**[0058]** A polyacrylate latex was prepared according to the procedure described in Example 1 except that the reactor was charged with 332.5 g water, 2.7 g PPS and 0.8 wt. % of the monomer pre-emulsion.

#### EXAMPLE 3

**[0059]** A polyacrylate latex was prepared according to the procedure described in Example 1 except that the reactor was charged with 331.4 g water, 2.7 g PPS, 1.8 g B-22 and 3.0 wt. % of the monomer pre-emulsion.

#### EXAMPLE 4 (CONTROL)

**[0060]** A polyacrylate latex was prepared according to the procedure described in Example 1 except that the monomer pre-emulsion was prepared by mixing 106.7 g water, 266.8 g 2-EHA, 245.5 g BA, 8.0 g MAA and 13.3 g AA with

7.1 g B-22, 4.3 g CO-660 and 2.1 g AOT. Also, the reactor was charged with 325.7 g water, 2.7 g PPS and 10.7 g B-22 and 3.0 wt. % of the monomer pre-emulsion before heat-up.

#### EXAMPLE 5

**[0061]** A polyacrylate latex was prepared according to the procedure described in Example 1 except that the monomer pre-emulsion was prepared by mixing 106.7 g water, 266.8 g 2-EHA, 138.7 g BA, 21.3 g MMA, 85.4 g MA, 8.0 g MAA and 13.3 g AA with 7.1 g B-22, 4.3 g CO-660 and 2.1 g AOT. Also, the reactor was charged with 325.7 g water, 2.7 g PPS, 10.7 g B-22 and 3.0 wt. % of the monomer pre-emulsion.

#### EXAMPLE 6 (CONTROL)

**[0062]** A polyacrylate latex was prepared according to the procedure described in Example 5 except that the monomer pre-emulsion was prepared by mixing 107.1 g water, 267.6 g 2-EHA, 187.3 g BA, 21.4 g MMA, 53.5 g MA and 5.4 g AA with 7.1 g B-22, 4.3 g CO-660 and 2.1 g AOT.

#### EXAMPLE 7

**[0063]** A polyacrylate latex was prepared according to the procedure described in Example 5 except that the monomer pre-emulsion was prepared by mixing 106.5 g water, 266.3 g 2-EHA, 170.4 g BA, 21.3 g MMA, 53.3 g MA, 8.0 g MAA and 13.3 g AA with 7.1 g FES-77, 4.3 g CO-660 and 2.1 g AOT. Also, the reactor was charged with 323.5 g water, 2.7 g PPS, 14.2 g FES-77 and 3.0 wt. % of the monomer pre-emulsion.

#### EXAMPLE 8

**[0064]** A polyacrylate latex was prepared according to the procedure described in Example 5 except that the monomer pre-emulsion was prepared by mixing 106.9 g water, 267.3 g 2-EHA, 171.1 g BA, 21.4 g MMA, 53.3 g MA, 8.0 g MAA and 13.3 g AA with 7.1 g L-22, 4.3 g CO-660 and 2.1 g AOT. Also, the reactor was charged with 327.9 g water, 2.7 g PPS, 7.1 g L-22 and 3.0 wt. % of the monomer pre-emulsion.

#### EXAMPLE 9

**[0065]** In a 2L jacketed glass reactor equipped with a reflux condenser, thermocouple and four-blade agitator, 1000.0 g of polyacrylate latex was prepared. Monomer pre-emulsion was prepared by mixing 157.3 g water, 266.4 g 2-EHA, 88.9 g BA, 62.3 g MA, 9.0 g MAA and 12.6 g AA with 25.2 g Hitenol BC-2020. The reactor was charged with 307.2 g water, 1.2 g PPS and 3.4 g Hitenol BC-2020. Separately, 66.4 g of PPS stock solution (2.5 wt. % concentration) was prepared in water. The reactor was heated with water. When the temperature reached 78°C, continuous addition of the monomer pre-emulsion and the PPS stock solution commenced at rates of 3.1 g/min and 18.1 ml/hr, respectively, for 200 minutes. The temperature was maintained at 83°C and the polymerization charge agitated continuously from 200 – 350 rpm. After the pre-emulsion addition was complete, the reactor temperature was held at 83°C and agitated for an additional 40 minutes. The reactor was cooled to 30°C and 0.11 g Kathon LX was added to the reactor and the pH was adjusted between 7-8 using 28% NH<sub>4</sub>OH aqueous solution.

#### EXAMPLE 10 (CONTROL: U.S. PAT. NO. 5,763,555)

**[0066]** In a 2L jacketed glass reactor equipped with a reflux condenser, thermocouple and four-blade agitator, 987.7 g of polyacrylate latex was prepared. Monomer pre-emulsion was prepared by mixing 197.3 g deionized water, 470.0 g 2-EHA, 10.0 g acrylamide (50%) (Cytec) and 25.2 g BDDM with 22.7 g DS-4 (22%) and 1.25 g SBC. The reactor was charged with 175 g deionized water. Separately, 25.3 g of sodium bisulfite stock solution (1.2 wt. % concentration) and 25.5 g PPS stock solution (3.9 wt. % concentration) were prepared in deionized water. The deionized water in the reactor was purged with nitrogen and heated with water. When the temperature reached 74°C, the nitrogen line was repositioned above the fluid and 21.8 g pre-emulsion, 1.3 g sodium bisulfite stock solution and 1.3 g of PPS stock solution were added to the reactor. When the temperature reached 78°C, continuous addition of the monomer pre-emulsion, the sodium bisulfite stock solution and the PPS stock solution commenced at rates of 3.9 g/min, 8.0 ml/hr and 8.0 ml/hr, respectively, for 180 minutes. The temperature was maintained at 78°C and the polymerization charge agitated continuously from 200 – 250 rpm. After the pre-

emulsion addition was complete, the reactor temperature was raised to 80°C and agitated for an additional 60 minutes. After the holding period, 3.8 g TBHP stock solution (13.2 wt. % concentration) and 3.8 g Formapon stock solution (13.2 wt. % concentration) were added to the reactor and mixed for fifteen minutes. The reactor was cooled to 30°C after which 28.0 g Kathon LX solution (3.6 wt. % concentration) was added to the reactor. The pH was adjusted between 7 – 8 using 28% NH<sub>4</sub>OH aqueous solution.

#### FORMULATION AND TESTING

**[0067]** The latex was formulated with CX-100 polyaziridine according to the levels listed in Table 1. The formulated latex sample listed as Example 11 (Control) in Table 1 is the latex of Example 9 with no added CX-100. The average particle size of each formulation was measured using a Horiba laser scattering particle size distribution analyzer model LA-910.

**[0068]** The formulated latex was direct coated on a 1.0 mil PET film and 1.0 mil corona treated BOPP film. The film was air dried for 15 minutes and heat dried at 90°C for 5 minutes. The coated film was laminated to a silicone release liner. The laminate construction was conditioned for 24 hours at 72±2°F and 50±2%RH (CTH conditions) prior to 180° dynamic peel and water whitening tests. Four 1" x 5.5" test strips were bonded to stainless steel panels for 24 hours (1 sample) and 1 week (3 samples). The one week samples were exposed to either CTH conditions, 70°C or 38°C/98% RH. Heat and humidity aged samples were reconditioned for 1 hour at CTH conditions prior to 180° dynamic peel testing. The tests were run in duplicate. Average Peel strength in lb/in was determined on an Instron Test Machine (Model No. 1125) by peeling a strip from a plate at an 180° angle. In reporting results, the mode of the peel failure is identified as follows: "A" meaning adhesive failure, i.e. adhesive entirely separates from the substrate, "C" meaning cohesive failure, i.e. the adhesive is left half on the substrate and half on the face stock, and "T" meaning transfer failure, i.e. the adhesive is all transferred to the substrate. A peel failure mode of "A" is acceptable. A peel failure mode of "C" or "T" is unacceptable as adhesive is left on the substrate.

**[0069]** The water whitening test was performed by immersing the adhesive coated BOPP film in water such that the adhesive layer was in direct contact with the water. After 24 hours of immersion, visual inspection of the coated film was performed. A zero-rating represents no whitening of the adhesive, whereas, a rating of five indicates a milky-white film. Numbers from 1 to 5 represent increasing levels of whitening. A rating of less than three is an acceptable level of adhesive water-whitening.

**[0070]** The results demonstrate that the crosslinked PSAs of the invention are removable (acceptable peel strength and adhesive failure mode) and water-whitening resistant (whitening rating less than 3), whereas the control samples are unacceptable because they either are not water-whitening resistant or they are not removable (have unacceptable adhesive failure mode).

Table 1

Example N .	1	2	3	4	5	6	7	8	9	10	11
	INV	INV	INV	CON	INV	CON	INV	INV	INV	CON	CON
<b>Surfactant:</b>											
L-22								0.8			
B-22	0.4	0.4	0.5	1	1	1					
FES-77							1.2				
BC-2020									1.3		1.3
DS-4										1	
CO-660	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8			
AOT	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3			
<b>Monomers:</b>											
2-EHA	50	50	50	50	50	50	50	50	60.7	94	60.7
BA	32	32	32	46	26	35	32	32	20.2		20.2
MMA	4	4	4		4	4	4	4			
MA	10	10	10		16	10	10	10	14.2		14.2
MAA	1.5	1.5	1.5	1.5	1.5		1.5	1.5	2		2
AA	2.5	2.5	2.5	2.5	2.5	1	2.5	2.5	2.9		2.9
acrylamide										1	
BDDM										5	
<b>Particle Size (nm)</b>	279	615	149	82	79	134	83	76	90	467	90
CX-100											
	2	2	2	2	2	2	2	2	2	0	0
<b>Whitening:</b>	0.5	2	0.5	3	0.2	5	0.1	0.2	0.1	5	0.1
<b>PET film:</b>											
PL24	0.26A	0.20A	0.47A	0.22A	0.55A	0.42A	0.51A	0.40A	0.41A	0.29A	1.92A
PL1W	0.24A	0.40A	0.56A	0.22A	0.52A	0.47A	0.57A	0.41A	0.48A	0.34A	2.40A
PL1W (70C)	0.50A	0.60A	1.23A	0.73A	1.12A	1.05A	1.16A	1.08A	1.07A	0.68A	2.40A
PL1W (98%)	0.60A	0.66A	0.69A	0.30A	0.87A	0.46A	0.65A	0.99A	0.81A	0.08A	2.87C
<b>BOPP film:</b>											
PL24	0.33A	0.23A	0.48A	0.34A	0.53A	0.51A	0.56A	0.47A	0.47A	0.35A	
PL1W	0.33A	0.42A	0.53A	0.34A	0.53A	0.44A	0.56A	0.49A	0.48A	0.34A	
PL1W (70C)	0.43A	0.47A	0.83A	0.79A	0.78A	0.83A	1.13A	0.83A	0.88A	0.32A	
PL1W (98%)	0.49A	0.60A	0.79A	0.41A	0.61A	0.42A	0.74A	0.61A	0.17A	0.08A	

INV = invention sample; CON = control sample